Journal of ELECTRONIC MATERIALS, Vol. 42, No. 12, 2013
DOI: 10.1007/s11664-013-2752-3
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Thermoelectric Properties of $Ca_{3-x}Dy_xCo_{3.95}Ga_{0.05}O_{9+\delta}$

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$Ca_3Co_4O_{9+\delta}$ and $Ca_{3-x}Dy_xCo_{3.95}Ga_{0.05}O_{9+\delta}$ (x = 0.05, 0.10) samples were prepared by conventional solid-state synthesis, and their thermoelectric properties measured at 25 K to 300 K. The x-ray diffraction patterns revealed that all the samples are single phase. The thermopower of all the samples was positive, indicating that the predominant carriers are holes over the entire temperature range. The highest power factor among all the samples (2.45 μW cm^{-1} K^{-2} at 132 K) was obtained for $Ca_{2.9}Dy_{0.1}Co_{3.95}Ga_{0.05}O_{9+\delta}$, being about 80% higher than that of the undoped sample. $Ca_{2.9}Dy_{0.1}Co_{3.95}Ga_{0.05}O_{9+\delta}$ had the highest dimensionless figure of merit of 0.033 at 300 K, representing an improvement of about 74% compared with undoped $Ca_3Co_4O_{9+\delta}$.

Key words: Thermoelectric materials, sintering, thermoelectric, thermal conductivity, x-ray diffraction, figure of merit

INTRODUCTION

Thermoelectric (TE) materials have been the focus of attention for protecting the environment by saving energy resources and reducing the release of CO_2 into the atmosphere. The efficiency of TE devices is determined by the dimensionless TE figure of merit of their materials, $ZT = S^2T/\rho\kappa$, where S, ρ, T, and κ are the Seebeck coefficient, electrical resistivity, absolute temperature, and thermal conductivity, respectively.[1,2] Wide attention has been focused on the exploration of TE materials recently. Layered cobalt oxides have attracted great attention since $NaCo_2O_4$ single crystal was found to exhibit good TE properties.[3] Recently, misfit cobalt oxides ($Ca_3Co_4O_{9+\delta}$) have been investigated extensively as potential TE materials because of their large S, low ρ, and low κ.[4–9] The crystal structure of the $Ca_3Co_4O_{9+\delta}$ system consists of two subsystems, viz. a distorted NaCl-type (Ca_2CoO_3) sublattice and a CdI_2-type (CoO_2) sublattice, alternately stacked along the c-axis.[10] Polycrystalline bulk $Ca_3Co_4O_{9+\delta}$ samples are still at a relatively low level of development for industrial application. Many attempts have been made to optimize the TE performance of $Ca_3Co_4O_{9+\delta}$ by either partially substituting cations or using appropriate fabrication methods such as hot pressing[11] or spark plasma sintering techniques.[12] Partial replacement of cations in $Ca_3Co_4O_{9+\delta}$ has been carried out on either the Ca site[13–19] or the Co sites.[5,8,20–22] Recently, our group reported the effect of Ga on the TE properties of the $Ca_3Co_{4-x}Ga_xO_{9+\delta}$ (x = 0.00, 0.05, 0.10, 0.20) system.[8] We have obtained the highest ZT value among the samples for $Ca_3Co_{3.95}Ga_{0.05}O_{9+\delta}$.[8] There are a few reports regarding the TE properties of the $Ca_{3-x}Dy_xCo_4O_{9+\delta}$ system.[9,23–25] To the best of our knowledge, there are no reports on simultaneous substitution of Ca and Co by Dy and Ga in the $Ca_3Co_4O_{9+\delta}$ system. Therefore, it is interesting to investigate the effect of simultaneous substitution of Dy at the Ca site and Ga at the Co site in the $Ca_3Co_4O_{9+\delta}$ system. In this paper, we report the low-temperature TE properties of the $Ca_3Co_4O_{9+\delta}$ and $Ca_{3-x}Dy_xCo_{3.95}Ga_{0.05}O_{9+\delta}$ (x = 0.05, 0.10) systems.

EXPERIMENTAL PROCEDURES

Polycrystalline samples of $Ca_3Co_4O_{9+\delta}$ and $Ca_{3-x}Dy_xCo_{3.95}Ga_{0.05}O_{9+\delta}$ (x = 0.05, 0.10) were synthesized by conventional solid-state reaction from $CaCO_3$, Co_3O_4, Dy_2O_3, and Ga_2O_3 powders. The powders were heated at 900°C for 24 h with

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(Received April 19, 2013; accepted August 19, 2013;
published online September 25, 2013)